Thermal decomposition of chemically treated cellulosic fibers

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Abstract   The thermal decomposition of cotton and hemp fibers were studied after mild alkaline treatments with tetramethyl-, tetraethyl-, and tetrabutylammonium hydroxides with the goal of modeling the chemical activation during carbonization of cellulosic fibers. The thermal decomposition was studied by thermogravimetry/mass spectrometry and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The treated samples decomposed in two temperature ranges during heating in the thermobalance. At lower temperature, tetraalkylammonium hydroxides (TAAH) ionically bonded to the cellulose molecules were decomposed; moreover, the alkaline agents initiated the partial decomposition of cellulose. Those fiber segments, which were not accessible for TAAH, decomposed at similar temperatures as the original cotton and hemp samples. It is known that quaternary ammonium hydroxides swell the cellulosic fibers; however, the results of this study proved that there was a chemical interaction between the alkaline swelling agents and cotton or hemp fibers at rather low temperatures (200-300 °C). The evolved products indicated that the alkaline chemicals reacted with the cellulose molecules and alkylated compounds were formed. This observation was confirmed by thermochemolysis experiments carried out by Py-GC/MS using tetramethylammonium hydroxide reagent. The thermochemolysis experiments under mild conditions resulted in the methylation of the glucoside units and levoglucosan, and no peeling reactions of the sugar units was observed as during strong alkaline conditions described in the literature.

Keywords   Cellulose, Biomass, Tetraalkyl ammonium hydroxide, TMAH, Carbonization, Pyrolysis, Thermogravimetry

Abbreviations

TG	Thermogravimetric curve
DTG	Differential thermogravimetric curve
T_{peak}	Temperature belonging to the maximum of the $-dm/dt$ curves
TG/MS	Thermogravimetry/mass spectrometry
Py-GC/MS	Pyrolysis-gas chromatography/mass spectrometry
RT	Retention time
M	Molar mass

THM	Thermally-assisted hydrolysis and methylation
TAAH	Tetraalkylammonium hydroxide
TMAH	Tetramethylammonium hydroxide
TEAH	Tetraethylammonium hydroxide
TBAH	Tetrabutylammonium hydroxide

Highlights

TAAH not only swells cellulosic fibers, but it is bonded chemically to the fibers.

TAAH moieties in the fibers decompose at 90 °C higher temperature than the pure alkaline chemicals.

The treated segments of the fibers release cellulosic products, as well, below 300 °C.

Methylated monomeric compounds are evolved from TMAH-treated fibers during pyrolysis.

Introduction

Biomass carbonization has been studied extensively using numerous feedstocks and various thermal techniques [1-3]. Carbonization of biomass produces pyrolysis oil, gas and charcoal, which is applied in various fields of the industry [3, 4]. Wood charcoal is used as a reductant in the metallurgical industry (mainly steel and ferrosilicon industry) [5]. Charcoal is among the most important renewable fuels (industrial and cooking fuel, syngas feedstock, and pyrotechnics). The term biochar refers to the black carbon produced from any biomass feedstock and used as a soil amendment to improve the agricultural soil fertility [6, 7] and applied for the pollution remediation [8].

Activated carbon is widely used to remove pollutants from gaseous and liquid materials. Activated carbon can be produced by physical or chemical activation [9]. During the physical activation, the biomass is carbonized at first and then the charcoal is activated [10]. Carbonization of biomass is carried out at high temperature in an inert atmosphere to remove the volatile matter and hence to reduce the oxygen content. The formed charcoal is then partially gasified at high temperature using steam or carbon dioxide to increase the pore volume and the surface area of the product.

In the chemical activation process generally one heat-treatment is applied, and the pore volume and surface area are enhanced by the use of impregnated catalysts (e.g., phosphoric acid, zinc chloride, sodium hydroxide) [11]. This process can also be performed in two stages. Dobele et al. [12, 13] used phosphoric acid as a dehydration catalyst in the first step and sodium hydroxide activator in the second step.

The carbonization of cellulosic fibers results in charcoals of fibrous character, which can be suitable for filtration and the removal of contaminants from waste water. Various fibrous plant materials have been suggested for the preparation of activated carbon [9, 14]. In this work, cotton and industrial hemp fibers were used for the preparation of activated carbon using chemical activation during the carbonization process.

The thermal decomposition of cellulose [15-18] and various cellulosic fibers [19-24] has been studied for a long time, yet the decomposition mechanism is not fully clarified. The decomposition reactions of cellulose are generally divided into two groups [25-27]. The fragmentation reactions produce low molecular mass products

(gases, water, aldehydes etc.) and char [28, 29], while the depolymerization reaction results in the formation of levoglucosan [30]. The dehydration and rearrangement reactions parallel with the depolymerization generate various pyran and furan derivatives.

The swelling effect of quaternary ammonium hydroxides on cellulose is well-known [31-33]. Bases of a molecular mass less than 150 are only swelling agents, while those of higher molecular mass are solvents for cellulose [31]. Tetramethylammonium hydroxide (TMAH) is a widely used reagent for the combined derivatization and pyrolysis method that can be designated as a thermally-assisted hydrolysis and methylation (THM) process [34]. THM applied with GC/MS detection of the products is especially useful for the structural elucidation of very complex and polar materials [35] such as natural resins, humic substances [36], soils, sediments [37] and lignocellulosic materials [34, 38, 39]. Model compounds were used to clarify the alkaline hydrolysis and methylating reactions of cellulose using TMAH during pyrolysis [40, 41]. The effect of TMAH and sodium hydroxide of low concentrations was studied on the thermal degradation of cellulose by Tanczos et al. [39]. It was concluded that the interaction with cellulose had a stabilizing effect on TMAH decomposition. The alkylating efficiency of various quaternary alkylammonium hydroxides were compared by Lehtonen et al. [36] on a macromolecular humic substance (fulvic acid) using Py-GC/MS and it was concluded that TMAH is the most suitable alkylating agent for the analytical pyrolysis of very complex humic substances, while TEAH and TBAH were not capable to alkylate all the hydroxyl groups.

The goal of this study was to model the carbonization of cellulosic fibers in the presence of activating agents. The chemical activation of cotton and industrial hemp fibers was performed by three tetraalkylammonium hydroxide additives. Small-scale carbonization was carried out using a thermobalance coupled to a mass spectrometer in order to reveal the decomposition mechanism under well-defined conditions. Furthermore, analytical pyrolysis was applied to get more chemical information about the carbonization processes.

Experimental

Materials

Two kinds of cellulosic fibers were used, bleached cotton wool containing >99% α-cellulose and mechanically cleaned industrial hemp. The water solutions of tetramethyl-, tetraethyl- and tetrabutylammonium hydroxide compounds were purchased from Alfa Aesar. The cellulosic fiber samples (1 g) were treated with 10 mL 10% water solutions of tetraalkylammonium hydroxides, and the samples were filtered and dried at room temperatures.

Methods

TG/MS

The TG/MS experiments were performed in a modified Perkin Elmer TGS-2 thermobalance coupled to a Hiden HAL 301/PIC2 quadrupole mass spectrometer. Approximately 4 mg fiber samples were measured in a platinum

sample pan in argon atmosphere using 140 mL min^{-1} flow rate. Reference experiments were performed with TMAH, TEAH, and TBAH placing 5 µL 10% water solutions into the sample pan. The thermobalance was purged by argon gas for 45 minutes before the experiments to remove the residual oxygen from the furnace. The samples were heated at a linear rate of 20 °C min^{-1} up to 900 °C. A portion of the volatile products was introduced through a heated glass-lined metal capillary into the mass spectrometer, where the ion intensities were monitored using electron impact ionization (EI) with 70 eV electron energy. The mass range of *m/z* 14-150 was scanned except the ions of the argon carrier gas.

Py-GC/MS

The pyrolysis experiments were carried out using a Pyroprobe 2000 (Chemical Data Systems, USA) connected on-line to an Agilent 6890/5973 GC/MS (Agilent Technologies, USA). About 0.7 mg samples were placed into the quartz tube of the pyrolyzer and were heated fast to 550 °C and kept there for 20 s. The carrier gas was helium, which flushed the volatile products onto the gas chromatographic column. The separation of the products was performed on an Agilent DB-1701 column (30m x 0.25 mm I.D. x 0.25 µm film thickness) held at 40 °C for 4 min, then heated at a 6 °C min^{-1} rate to 280 °C and kept there for 7 min. The mass spectrometer operated in EI mode with 70 eV and the mass range of 14-500 Da was scanned.

THM experiments were performed on 1 mg cotton fiber applying 10 µL 10% solution of TMAH. After drying, the sample was pyrolyzed at 550 °C for 20 s. This sample is named fresh-treated cotton. The parameters of GC/MS analysis were the same as for the other samples.

Results and discussions

Thermal decomposition of the untreated cotton and hemp samples

The thermal decomposition of cotton wool occurred in the temperature range between 300 and 420 °C as shown in Figure 1.
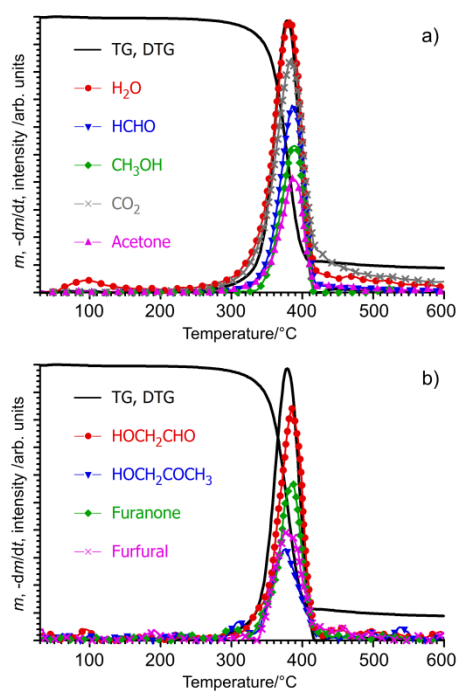
Fig. 1 TG/MS curves of untreated cotton. TG, DTG and the evolution profiles of a few important products: *m/z* 18, water; *m/z* 30, formaldehyde; *m/z* 32, methanol; *m/z* 44, carbon dioxide; *m/z* 58, acetone; *m/z* 60, hydroxyacetaldehyde; *m/z* 74, hydroxypropanone; *m/z* 84, furanone; *m/z* 96, furfural

The maximal decomposition rate took place at 378 °C and the char residue determined at 900 °C was 8.1% as presented in Table 1. The cotton sample contained adsorbed water, which evaporated mostly at room temperature before the experiment during purging the thermobalance by dry argon gas. The residual moisture content (about 1%) evaporated at around 100 °C as confirmed by the mass spectrometric curve of water (Fig. 1a). Cellulose represents the major component of the cotton sample, which decomposes via various decomposition routes [15, 26, 27]. One group of the reactions is fragmentation reactions producing gases, water, and char. Fig. 1a presents the most significant low-molecular mass products measured by TG/MS. Water, formaldehyde and methanol were probably derived from the cleavage of the hydroxyl and hydroxymethylene side groups of cellulose molecules. The scission of the glucopyranose rings led to the formation of other oxo-compounds, such as acetone (Fig. 1a), hydroxyacetaldehyde, and hydroxypropanone (Fig. 1b). The formation of carbon dioxide can be explained by the oxidation of C-O groups. The other type of reactions is the depolymerization of the carbohydrate chains producing primarily levoglucosan (1,6-anhydro-β-D-glucopyranose). We could not detect levoglucosan by TG/MS due to its high polarity and the condensation in the transfer line. The dehydration and the rearrangements of the glucopyranose rings resulted in the formation of furan derivatives, as the evolution of furanone and furfural illustrates in Fig. 1b.

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Table 1 Effect of various treatments on the temperature of maximal decomposition rate and the char yield during the thermal decomposition of cotton and hemp

Samples	Cotton		Hemp	
	T_{peak} /°C	Char yield* /w%	T_{peak} /°C	Char yield* /w%
Untreated	378	8.1	366	12.7
Washed	370	5.4	363	13.3
TMAH-treated	369	16.8	347	12.2
TEAH-treated	380	13.4	367	13.1
TBAH-treated	379	12.5	363	10.6

* Determined at 900 °C.

The thermal decomposition of hemp fiber proceeded similarly as that of cotton fiber. About 2% moisture remained in hemp after the purging period, as the TG curve and the evolution of water demonstrates in Fig. 2a. The decomposition of the major component, cellulose occurred at about 10 °C lower temperature than in case of cotton as the T_{peak} data indicate in Table 1. The char yield was 12.7%, which is significantly higher than that of cotton.
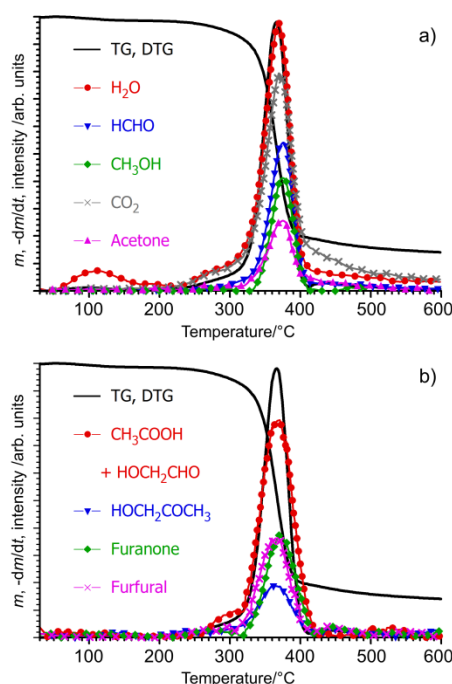

Fig. 2 TG/MS curves of untreated hemp. TG, DTG and the evolution profiles of a few important products: *m/z* 18, water; *m/z* 30, formaldehyde; *m/z* 32, methanol; *m/z* 44, carbon dioxide; *m/z* 58, acetone; *m/z* 60, acetic acid and hydroxyacetaldehyde; *m/z* 74, hydroxypropanone; *m/z* 84, furanone; *m/z* 96, furfural

The increased char yield can be explained by the lignin content of hemp, which produces large amount of char. The decomposition started at lower temperature (at about 250 °C) than in case of cotton (at about 300 °C),

which can be due to the lignin and the hemicellulose content of hemp. The evolution curves of water and carbon dioxide confirm the decomposition of these components above 250 °C (Fig. 2a).

Furthermore, the evolution profile of the *m/z* 60 ions also shows a peak at about 300 °C (Fig. 2b), which can be attributed to the release of acetic acid from the acid groups of hemicellulose and lignin. The main peak of the *m/z* 60 ion curve at about 370 °C represents hydroxyacetaldehyde, which is one of the main fragmentation products of cellulose. Although the *m/z* 60 ions represent both acetic acid and hydroxyacetaldehyde, the identification is possible on the basis of the characteristic fragment ions, *m/z* 45 and 31, respectively. The decomposition of cellulose component of hemp proceeds similarly to that of cotton, but the intensity of the higher molecular mass products is lower in agreement with the lower cellulose content.

Thermal decomposition of quaternary ammonium hydroxides

Before studying the interaction between the quaternary ammonium hydroxides and the cellulosic fibers, the thermal decomposition of tetraalkylammonium hydroxides has been analyzed by TG/MS. Figure 3 shows the TG/MS plots of tetramethyl- and tetraethylammonium hydroxide. The decomposition of tetraethyl- and tetrabutylammonium hydroxide is quite similar; therefore the decomposition of the former is only presented here. As Fig. 3a demonstrates, TMAH released about 20% water below 100 °C, which originated apparently from the crystalline water bonded to TMAH. It is likely that the water solvent was released during purging the furnace before the experiment. The decomposition of TMAH proceeded by dissociation reactions leading to the formation of trimethylamine and methanol between 100 and 200 °C, as the evolution profiles of the molecular ions (*m/z* 59 and 32) indicate in Fig. 3a. The decomposition of TEAH occurred at about 50 °C lower temperature with the evolution of triethylamine and ethanol. Fig. 3b shows the molecular ion of triethylamine (*m/z* 101) and the main fragment ion of ethanol (*m/z* 31, hydroxymethyl) since the molecular ion (*m/z* 46) has very low intensity in the mass spectrum of ethanol. None of the tetraalkylammonium hydroxides produced char residue indicating that no secondary reactions took place during decomposition.
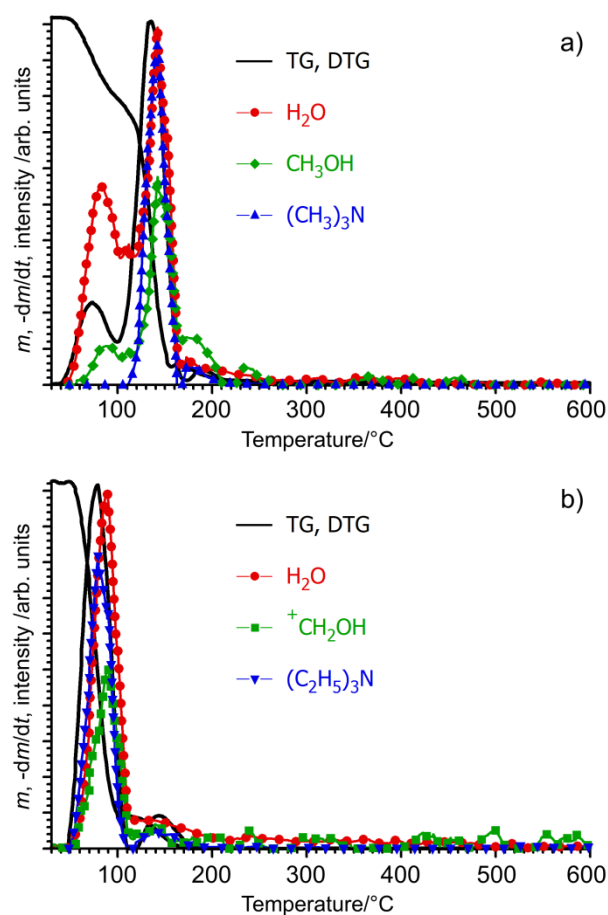
Fig. 3 TG/MS curves of (a) TMAH and (b) TEAH. TG, DTG and the evolution profiles of the products: *m/z* 18, water; *m/z* 31, hydroxymethyl fragment ion; *m/z* 32, methanol; *m/z* 59, trimethylamine; *m/z* 101, triethylamine

Effect of quaternary ammonium hydroxides on the thermal behavior of cotton and hemp

Figure 4 presents the thermogravimetric curves of the untreated and treated cotton samples. As the tetraalkylammonium hydroxide treatments were performed in water solution, a reference sample was prepared using pure water, as well. TG (Fig. 4a) and DTG (Fig. 4b) curves show that the difference between the thermal behavior of untreated and water treated (washed) samples is rather small. The peak temperature of the DTG curve is only 8 °C lower (Table 1); however, the char yield reduced by 2.7% that can be explained by the removal of some impurities from the cotton fiber.
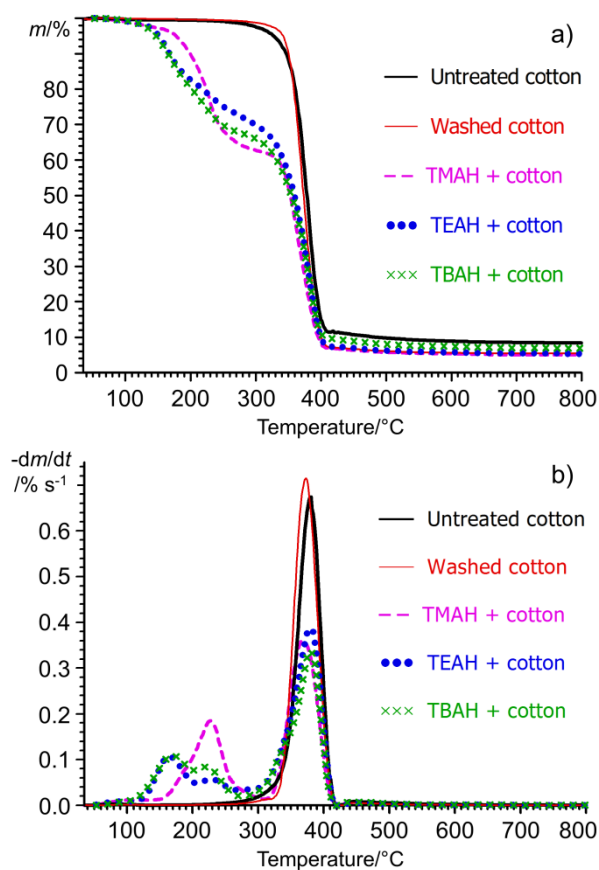
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Fig. 4 (a) TG and (b) DTG curves of untreated and treated cotton

The thermal decomposition of the alkali treated cotton samples occurred in two main stages (Fig. 4). The low-temperature mass loss below 300 °C (about 30-35%) can be attributed mainly to the release of alkaline chemicals bonded to the cellulose fibers. Cellulose molecules degraded in the main devolatilization step between 300 and 420 °C, similarly to the untreated and washed cotton samples. The largest difference between the decomposition temperatures (T_{peak}) of all cotton samples is only 11 °C (Table 1). It can be established that there is an interaction between the alkaline chemicals and the cotton fibers because the formation of volatile products occurred at about 90 °C higher temperature than the decomposition of the pure chemicals (Fig. 3). TMAH-treated segments of cotton were thermally more stable than TEAH- and TBAH-treated cotton segments, which is in agreement with the stability of the pure alkaline chemicals. The maximum of the DTG curve is 230 °C for the first decomposition step of TMAH-treated cotton and it is 160 °C for TEAH- and TBAH-treated cotton. It indicates that the interaction of cellulose is stronger with the smaller TMAH molecules than with the larger TEAH and TBAH molecules. The more compact TMAH molecules probably were able to penetrate into the non-polar intermolecular sheets of cellulose as it was discussed by Tóth et al. [33].

As Figure 5 and Table 1 illustrate, the washed and untreated hemp samples decomposed very similarly due to the cleaning of hemp fibers before use. Hemp sample absorbed higher amount of quaternary ammonium hydroxides than cotton as the comparison of Figures 4 and 5 indicates. The mass loss up to 300 °C amounts to 50-60% of the alkaline-treated samples. The DTG curves of TEAH- and TBAH-treated hemp show that the first decomposition step involves two processes suggesting that there are weaker and stronger interactions between

the chemicals and hemp. The second peak or shoulder coincides with the decomposition of TMAH-treated hemp. Above 300 °C, apparently the residual hemp fibers degraded with T_{peak} temperatures between 347 and 367 °C.
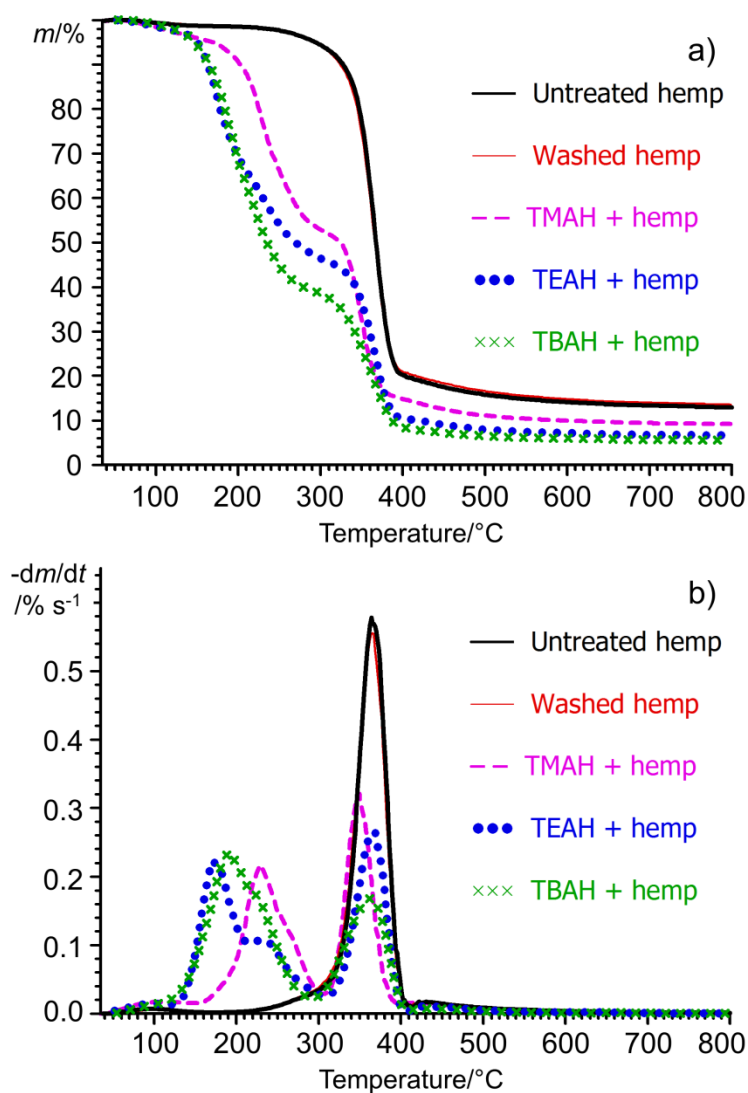

Fig. 5 (a) TG and (b) DTG curves of untreated and treated hemp

Decomposition products of TMAH-treated fibers

The thermal decomposition of the quaternary alkylammonium hydroxide-treated samples proceeded similarly, therefore the TG/MS curves of TMAH-treated samples are only presented here. Figure 6 shows the evolution profiles of a few characteristic compounds produced during the thermal decomposition of TMAH-treated cotton (Fig. 6a) and hemp (Fig. 6b). TMAH was applied to the fibers from water solutions, hence the amount of adsorbed water increased in both samples significantly in comparison with the untreated samples (Figs. 1a, 2a, and 6). After the evaporation of the moisture content, probably the crystalline water bonded to TMAH residues was released at about 200 °C, since the crystalline water of TMAH is released just before the decomposition of TMAH [39]. The water evolution peak at about 240 °C accompanies the decomposition of the TMAH-treated

segments, while the main water peak can be attributed to the scission of the hydroxyl functional groups of cellulose in cotton and hemp at about 370 and 350 °C, respectively.
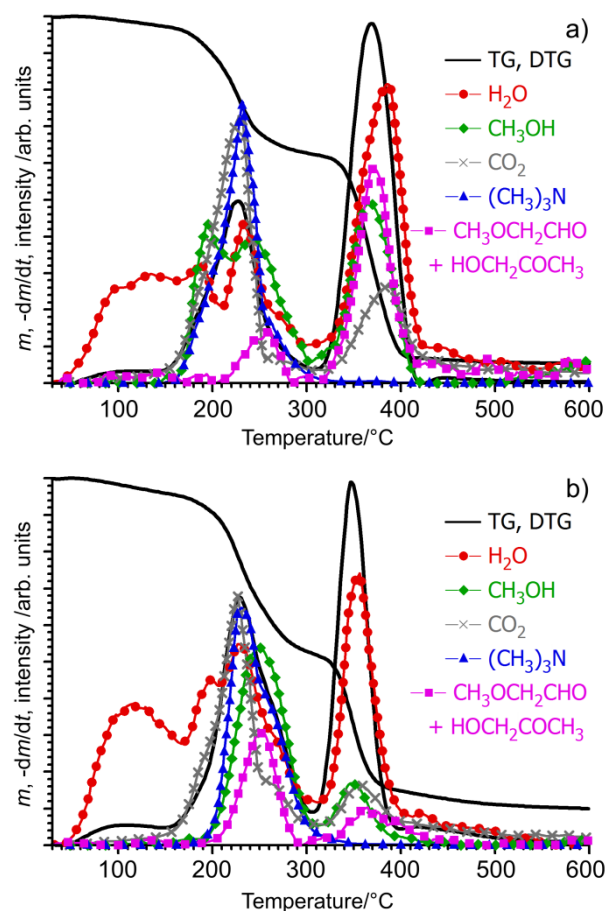

Fig. 6 TG/MS curves of (a) TMAH-treated cotton and (b) TMAH-treated hemp. TG, DTG and the evolution profiles of a few important products: *m/z* 18, water; *m/z* 32, methanol; *m/z* 44, carbon dioxide; *m/z* 59, trimethyl amine; *m/z* 74, 2-methoxyacetaldehyde and hydroxypropanone

The release of carbon dioxide from TMAH-treated fibers started at about 150 °C, when the temperature is increased in the thermobalance. Its formation indicates the oxidation of cellulose in the presence of the alkaline swelling agents; for example, the terminal ─CH_2OH groups might have been oxidized to produce CO_2. The devolatilization of TMAH residues occurred between 150 and 300 °C; however, the evolution curves of various compounds did not coincide indicating that more decomposition reactions took place in this temperature range. Pure TMAH decomposed by the simultaneous release of trimethylamine and methanol (Fig. 3a); however, the formation of these products occurred at different temperatures from the TMAH-treated fibers (Fig. 6). This observation proves that chemical reaction took place between TMAH and the fibers. Trimethylamine evolution was centered at about 230 °C from both samples, although cotton started to release it at a lower temperature, while the evolution curve of hemp has a shoulder at higher temperature. It means that tetramethylammonium ions are bonded to various sites, which have slightly different thermal stability. Methanol formation occurred at about 250 °C from both samples; however, TMAH-treated cotton released methanol in a separated peak at about 200 °C, as well. TMAH treatment caused methylation of certain cellulose moieties during thermal

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decomposition, and these reactions took place at about 100 °C lower temperature than the decomposition of pristine cellulose. It is proved by the formation of methoxyacetaldehyde at about 250 °C from both samples. Hydroxyacetaldehyde is a typical product of cellulose formed by the fragmentation of the glucopyranose rings between 320 and 420 °C, as shown in Figs. 1b and 2b. Its methylated derivative, methoxyacetaldehyde was formed from the TMAH-treated samples at as low temperature as 200-300 °C. Apparently not only the original hydrogen-bonded microcrystalline structure of cellulose was disrupted during swelling in the alkaline chemicals, but chemical reactions took place between TAAH and the fibers. Higher yield of methoxyacetaldehyde was formed from hemp (Fig. 6b) than from cotton (Fig. 6a), which indicates the higher methoxy content of hemp. As discussed above, the hemp sample absorbed higher amount of TMAH than cotton and hence more methoxy groups were formed in hemp.

Cellulose segments that were not accessible for the alkaline agents decomposed above 300 °C similarly as the original cotton and hemp samples. There was no trimethylamine evolution in this temperature range confirming that the residues of the alkylating agents decomposed below 320 °C. Hemp took up higher amount of TMAH and released more volatiles in the first decomposition range, therefore it produced lower amount of volatile products in the second decomposition stage than TMAH-treated cotton. Figure 6 shows the evolution curve of the *m/z* 74 ions, which represent the molecular ions of two products, methoxyacetaldehyde and hydroxypropanone. Their identification was based on the pyrolysis-GC/MS results, as discussed below. Methoxyacetaldehyde was evolved between 200 and 300 °C, as detailed above. Hydroxypropanone was formed from the cellulose chains during the fragmentation of the pyranose rings. Its yield was higher from cotton because the cellulose content of cotton fibers is higher than that of hemp.

Effect of TMAH treatment on the pyrolysis products of cotton

Pyrolysis-GC/MS experiments have been carried out on the untreated and treated samples in order to get more information on the product distributions and the mechanisms. The TG results indicated that the decomposition processes were ended by 550°C, therefore this was chosen as the pyrolysis temperature. Figure 7 presents the pyrolysis-gas chromatograms (pyrograms) of untreated and TMAH-treated cotton samples as examples for the pyrolytic behavior of cellulosic fibers. In addition to the pyrolysis of the previously treated TMAH-cotton sample, we carried out another experiment for comparison, where TMAH was added to the cotton sample just before the pyrolysis (fresh TMAH-treated sample). Fig. 7a shows the pyrogram of the untreated cotton wool, and Table 2 lists the identification of the major compounds. As it is well-known [15], the main decomposition product of cellulose is levoglucosan (**22**), which is formed by depolymerization, so it can be considered as the monomer of cellulose. The release of 1,6-anhydro-β-D-glucofuranose (**23**) proves that transformation of the pyranose rings occurs into furanose rings, to some extent. The rearrangement and dehydration reactions of the pyranose units lead to the evolution of furan derivatives (**11, 16**). The dehydration of the monomeric units results in the formation of a few bicyclo-compounds (**13-15**) and pyran derivative (**19**). Hydroxyacetaldehyde (**8**) and other oxo-compounds (**6, 9, 10**) are formed during the scission of the pyranose rings of cellulose.

The TMAH-treated cotton sample (Fig. 7b) released large amounts of trimethylamine (**3**) and methanol (**4**) originating from TMAH. Besides gases and water, levoglucosan (**22**) was the most significant product from the

cellulose molecules. Furthermore, a new peak appeared in the pyrogram, methyl-2-O-methyl-α-D-glucopyranoside (**20**), which was formed by methylation of the pyranoside bond of cellulose and the hydroxyl group at position 2. Trace amount of dimethyl-methyl-glucopyranoside was also formed (**18**). The pyrogram of the fresh treated cotton sample (Fig. 7c) shows more methylated compounds, which are methyl-D-glucopyranoside (**21**), its methylated derivatives (**18, 20**), and dimethyllevoglucosan (**17**). Furthermore, the pyrogram has two higher molecular mass compounds (**24, 25**), which are possibly methylated dimers.
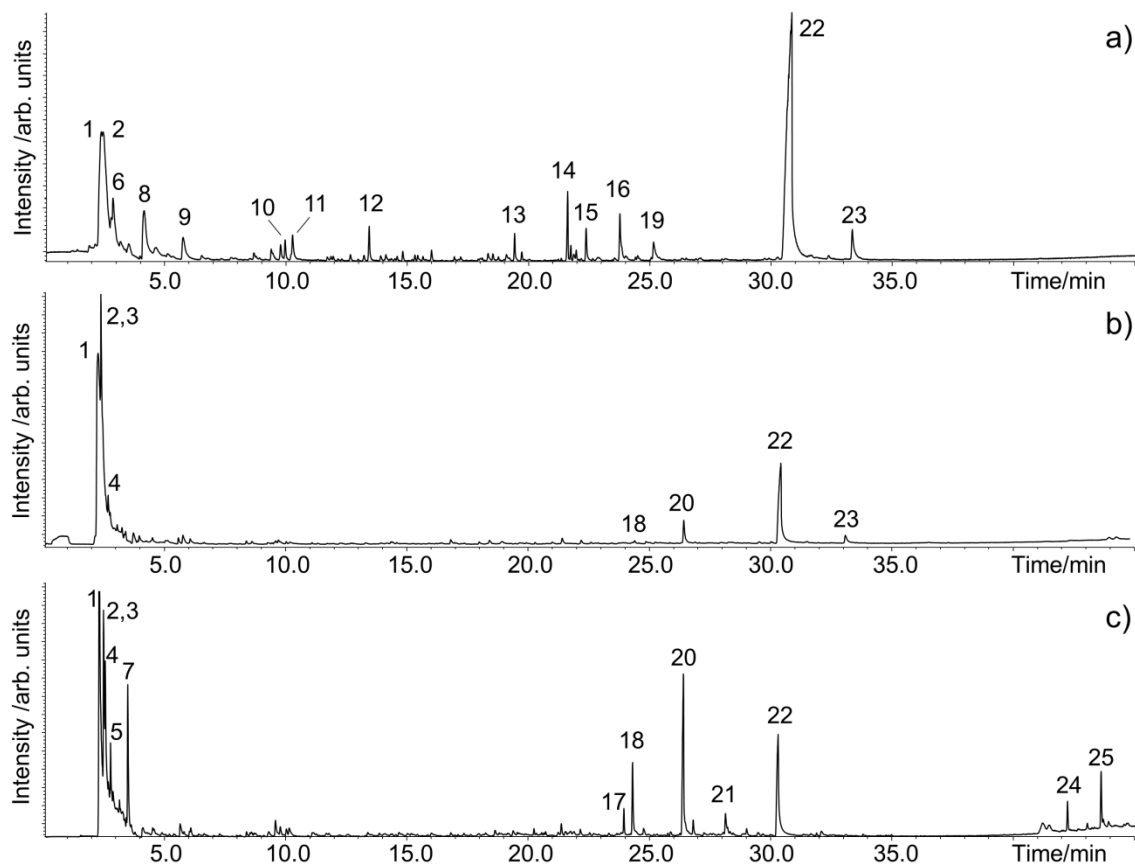

Fig. 7 Pyrolysis gas chromatograms of (a) untreated, (b) TMAH-treated, and (c) fresh TMAH-treated cotton. The identification of the numbered peaks is found in Table 2

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Table 2 Identification and the main GC/MS characteristics of the pyrolysis products of untreated and TMAH-treated cotton (see Fig. 7)

No.	RT /min	Compound	M /g mol^{-1}	Characteristic MS ions
1	2.34	Gaseous products (CO_2, CO, HCHO)		
2	2.41	Water	18	18, 17, 16
3	2.48	Trimethylamine	59	58, 59, 42, 30
4	2.55	Methanol	32	31, 32, 29, 15
5	2.77	2-Propenal	56	56, 27, 55, 29
6	2.83	Butanal	72	43, 29, 15, 72
7	3.48	Methoxyacetaldehyde	74	45, 29, 44, 74
8	4.09	Hydroxyacetaldehyde	60	31, 29, 32, 60, 42
9	5.71	1-Hydroxy-2-propanone	74	43, 31, 74, 15
10	9.91	2-Hydroxy-butanal-3-one	102	43, 31, 102, 29
11	10.23	2-Furanaldehyde	96	96, 95, 39, 29, 67
12	13.38	1,2-Cyclopentanedione	98	98, 55, 42, 69, 41
13	19.37	Levoglucosenone (6,8-Dioxabicyclo [3.2.1] oct-2-en-4-one)	126	98, 68, 96, 39, 53
14	21.57	(1R)-1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	144	43, 41, 69, 70, 116
15	22.33	1,4:3,6-Dianhydro-α-D-glucopyranose	144	69, 57, 29, 41, 144
16	23.73	5-Hydroxymethylfurfural	126	97, 126, 41, 39, 69
17	23.95	Dimethyllevoglucosan	190	101, 45, 99, 127, 75, 71
18	24.31	Methyl-3,6-O-dimethyl-D-glucopyranoside	222	88, 87, 73, 103, 45
19	25.15	2-Hydroxymethyl-5-hydroxy-2,3-dihydro-(4H)-pyran-4-one	144	144, 87, 97, 29, 57
20	26.40	Methyl-2-O-methyl-α-D-glucopyranoside	208	74, 87, 59, 57, 45
21	28.13	Methyl-D-glucopyranoside	194	74, 103, 73, 59, 45
22	30.81	Levoglucosan	162	60, 57, 73, 29, 42
23	33.27	1,6-Anhydro-β-D-glucofuranose	162	73, 69, 43, 44, 61
24	42.24	Methylated dimer		88, 173, 45, 233, 205
25	43.62	Methylated dimer		88, 219, 45, 173, 74, 205

Methylation of the typical fragmentation product, hydroxyacetaldehyde was observed during THM resulting in the formation of methoxyacetaldehyde (**7**) similarly to the TG/MS experiments. Comparison of the dry and fresh treated samples shows that the methylating effect was significantly higher when TMAH was added to cotton just before the pyrolysis. Although the same mass ratio was applied (TMAH:cotton=1:1) during both treatments, the residual TMAH solution was filtered in the larger scale experiment, while all the solution remained in the pyrolysis tube during the THM experiment, and probably more TMAH was available for the reactions. It is possible that the higher water content of the fresh sample also played role in the pyrolysis and methylation reactions. It should be noted that the formation of saccharinic and isosaccharinic compounds were described in the literature during THM of cellulose [35, 38, 40, 41]; however, we could not detect these products, which can

be explained by the different objectives and the experimental conditions. The goal of the published studies was to methylate the pyrolysis products completely, and hence very strong alkaline conditions were applied: 25% TMAH was used in the mass ratio of TMAH:cellulose≥100:1. We used much milder conditions and apparently different reactions took place. The glucopyranose rings remained intact during the TMAH treatment, the alkali ions caused no peeling reactions of the sugar units and only partial methylation of the hydroxyl groups occurred. During pyrolysis, transesterification of the ether groups took place: the pyranoside bonds cleaved and the oxygen residues were methylated. Thus, the most important products were methylglucopyranosides.

Conclusions

Quaternary ammonium hydroxides (methyl, ethyl, and butyl) were used as chemical activating agents in the carbonization process of cotton wool and hemp fiber. The carbonization was modeled using slow heating rate in the TG/MS and high heating rate in the pyrolysis-GC/MS experiments. Significant increase in the char yield was achieved using alkali-treated cotton wool, while the char yield of hemp fiber was not much influenced by the treatments.

Tetraalkylammonium hydroxides decomposed between 50 and 200 °C with the evolution of trialkylamines and alcohols. TEAH and TBAH were rather labile degrading at about 80 °C, while TMAH decomposed at about 140 °C. The treated cotton and hemp fibers presented two main decomposition steps. The first process can be attributed to the elimination of the alkaline chemicals from the fibers by dissociation to amines and alcohols; however, partial decomposition of the treated cellulosic segments occurred, as well. Hydroxyacetaldehyde, the most significant fragmentation product of the pyranose rings, was methylated by TMAH and methoxyacetaldehyde was detected by TG/MS at rather low temperatures between 200 and 300 °C. In the second stage of decomposition, no amine compounds were formed. Those cellulosic fibers, which have not been accessible for the alkaline chemicals, decomposed above 300 °C similarly to the untreated cotton and hemp samples during the TG/MS experiments.

The higher molecular mass products were analyzed using pyrolysis-GC/MS. The previously TMAH-treated, dried cotton sample produced methylated methylglucopyranoside derivatives in addition to levoglucosan. However, the majority of the methylating agent released methanol and trimethylamine during pyrolysis at 550 °C. When the thermochemolysis was carried out on-line in the pyrolyzer, more methylated products were observed probably due to the higher amount of the alkylating agent and the higher water content. Three compounds were identified as methylglucopyranosides, and one compound was formed by the methylation of levoglucosan. Two compounds were observed with rather high molecular mass fragment ions, which were possibly methylated glucose dimers. It was concluded that the alkaline pretreatment with tetramethylammonium hydroxide under mild conditions resulted only in methylation of the glucopyranoside segments and hydroxyacetaldyde, and no peeling reactions of the sugar units took place as described in the literature under strong alkaline conditions.

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